

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to Cyclic Imides

We, GENERAL ANILINE & FILM CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America, of 140 West 51st Street, City, County and State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process of alkylating 5- and 6-membered cyclic imides and to the products resulting therefrom.

In particular, the invention relates to a process for alkylating 5- and 6-membered cyclic imides with α -olefins in the presence of an organic peroxide as an alkylation initiator to produce a large variety of useful alkylated products which may be employed as such or in organic synthesis.

In accordance with the process of the present invention an α -olefin of at least 2 carbon atoms, or a halo, hydroxy or cyano derivative thereof, is reacted with a 5- or 6-membered cyclic imide as hereinafter defined in the presence of an organic peroxide as an initiator. The alkylation reaction is readily accomplished by heating at a pressure in excess of atmospheric pressure a mixture consisting of 0.01 to 10 molar proportions of an α -olefin of at least 2 carbon atoms or the said derivative thereof and one molar proportion of a 5- or 6-membered cyclic imide in the presence of 0.02 to 0.3 molar proportions of an organic peroxide per mole of an α -olefin at a temperature of 100–200°C. for preferably 2 to 48 hours. The 5- or 6-membered cyclic imide may be used in

excess to control the degree of alkylation. If an excess is used, it is removed by precipitation and filtration after completion of the alkylation reaction.

The alkylation reaction may also be conducted in solution of an organic solvent common to the cyclic imide and α -olefin. As solvents we found that various alcohols such as methanol, ethanol, propanol, isopropanol, butanol, *sec*-butanol, amyl alcohol, hexanol, 2-ethyl-1-hexanol, ethylene glycol, 1,2-butanediol or 1,4-butanediol are very effective. Other solvents such as diacetone alcohol, diethylene glycol or ethylene glycol monomethyl ether acetate may also be employed. Any organic solvent may be used if it is a liquid, forms a solution with the cyclic imide and alkylated cyclic imide and is less susceptible to alkylation than under the cyclic imide under the reaction conditions.

The amount of organic solvent employed is not critical. Any amount which will yield a solution of the cyclic imide, α -olefin and alkylated cyclic imide will suffice. For every part by weight of cyclic imide from 2 to 10 parts of organic solvent, either by volume or by weight, are generally sufficient to yield a workable solution.

As an initiator for the alkylation reaction we can employ any one of the known organic peroxides normally employed as initiators in chemical reactions such as, for example, *t*-butylperbenzoate, di-benzoyl peroxide, benzoyl hydroperoxide, *t*-butyl - hydroperoxide, *t*-butyl perphthalic acid, *p*-chlorobenzoyl peroxide, *t*-butyl peracetate, di-*t*-butyl peroxide, di-*t*-amyl peroxide, bis-(triethylmethyl)peroxide or *t*-butyl - pentamethyl ethyl peroxide.

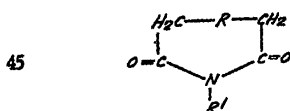
Where alkylated 5- and 6-membered

cyclic imides of a low degree of alkylation are desired and a low molecular weight olefin is used, the alkylation reaction may be conducted in the presence of any one of the

5 aforementioned alcohols.
Where it is desired to prepare a solution of the alkylated 5- or 6-membered cyclic imide in a mineral oil or a lubricating oil of a paraffinic stock, the initial alkylation reaction may be conducted in the presence of a higher boiling aliphatic alcohol such as, for example, hexanol. When the desired degree of alkylation has been obtained, the reaction mixture is subjected to vacuum distillation and the removed higher boiling alcohol may be replaced by a saturated aliphatic hydrocarbon having a boiling point higher than the alcohol. After the alcohol has been removed there is obtained a solution of the alkylated cyclic imide in solution of the aliphatic hydrocarbon.

Where low-boiling α -olefins of from 2 to 6 carbon atoms and fluoro- or chloro-fluoro α -olefins are employed as the alkylating agents, the organic peroxide catalyst, preferably di-*t*-butyl peroxide, and the solution of the cyclic imide are introduced into a stainless steel rocker bomb. The low-boiling α -olefin or fluoro- or chloro-fluoro α -olefin is then charged into the bomb and the bomb heated and maintained at a temperature of from 110° to 140°C. for 5 to 28 hours. The pressure developed in the bomb may range from 100–1000 psi. After cooling to room temperature the contents of the bomb are discharged into any suitable vacuum distillation equipment to remove the solvent and the residual product recovered as a solid or a viscous fluid.

40 The 5- and 6-membered cyclic imides which are alkylated with an α -olefin in accordance with the present invention are characterized by the following general formula:



wherein R represents either a single bond joining the two methylene ($-\text{CH}_2-$) groups or an oxy or methylene group and R' represents hydrogen, and alkyl group of from 2 to 18 carbon atoms inclusive, a hydroxy alkyl group or an alkylaminoalkyl group wherein the alkyl contains from 1 to 6 carbon atoms inclusive.

55 The following cyclic imides are illustrative of cyclic imides which may be alkylated in accordance with the present invention: succinimide, N-methyl succinimide, diglycolyl-imide, N-methyl diglycolylimide, glutarimide, N-methyl glutarimide.

Any α -olefin having a molecular weight from about 28 to as high as 2500 may be employed in the alkylation of the 5- and 6-membered cyclic imides. Thus, α -olefins ranging from ethene (ethylene) to polybutenes having molecular weights from 400 to 2500 may be employed. As examples of such α -olefins the following are illustrative; ethene, propene, 1-butene, 1-pentene, 2-ethyl-1-butene, 2-methyl-1-pentene, 1-hexene, 5-methyl-1-hexene, 2-methyl-1-pentene, 1-hexene, 5-methyl-1-hexene, 2-methyl-1-pentene, 3-ethyl-1-pentene, 1-heptene, 1-octene, 1-nonene, 2-ethyl-1-hexene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-cicosene, 1-docosene, 1-tetracosene, 1-pentacosene.

Instead of employing any one of the foregoing individual α -olefins, a mixture of commercially available linear α -olefins produced by cracking petroleum wax or by polymerizing lower olefins may also be used as the alkylating agent. The commercial product composition contains a mixture of linear olefins. Such a mixture may contain linear olefins ranging from 6 to 8 carbon atoms inclusive, 8 to 12 carbon atoms inclusive, 10 to 12 carbon atoms inclusive, 12 to 16 carbon atoms inclusive, 16 to 20 carbon atoms inclusive and 20 to 42 carbon atoms inclusive. For example, the commercial product composition of linear heptene having 92% of mono-olefins contains 89% of α -heptene, 6% of α -hexene and 5% of α -octene based on the mono-olefin basis. By careful distillation of the commercial product composition substantially individual α -olefins are obtained which may be used as the alkylating agent.

While linear α -olefins are preferred because of their commercial availability, we have found that the numerous isomers of α -olefins ranging from 1-pentene to 1-pentacosene as well as polybutenes may also be employed in the alkylation reaction. The only requirement is that the isomer should contain an ethylenic unsaturation in the α -position thereof.

Chloro-fluoro α -olefins such as, for example, dichlorovinylidene fluoride ($\text{CCl}_2=\text{CF}_2$), chlorovinylidene fluoride ($\text{CHCl}=\text{CF}_2$), chlorotrifluoroethylene ($\text{CClF}=\text{CF}_2$), tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$), vinylidene fluoride ($\text{CH}_2=\text{CF}_2$) may be used to advantage in the present alkylation reaction.

By the proper choice of alkylating agent and the degree of alkylation, it is possible to obtain alkylated products which are soluble in polar solvents, such as alcohols or which are soluble in aliphatic hydrocarbons of from 6 to 60 carbon atoms inclusive, including isomers thereof, and in mineral and lubricat-

ing oils having a Saybolt viscosity of from C_{15-20} using one to three moles in excess of succinimide, diglycolylimide or glutarimide, the adducts would constitute the entire product. Multiple alkylation usually occurs if the cyclic imides are not used in excess.

The alkylation occurs in the 5- and 6-membered cyclic imide primarily in the alpha (to carbonyl) position. In the case of the alkylation of succinimide or N-methyl succinimide with an α -olefin such as, for example, 1-octene, the resulting alkylated product is primarily the 3-octyl succinimide, or N-methyl-3-octyl succinimide.

In the alkylation of 5- and 6-membered cyclic imides with α -olefins in accordance with the invention, more than one mole of the latter can react with each mole of the cyclic imide. For example, with an α -olefin

EXAMPLE 1

3-Octyl succinimide

Apparatus: One-litre four-necked flask equipped with stirrer, nitrogen inlet, thermometer and reflux condenser.

The flask was charged with nitrogen and then the following ingredients charged and heated:

Succinimide	=	396.0 grams (4.0 moles)
1-Octene	=	90.0 grams (0.8 mole)
Methyl Isobutyl Carbinol	=	400 mls.
Di- <i>t</i> -butyl Peroxide	=	15.0 grams (0.1 mole initial)

The mixture was heated and maintained at reflux (124°—143°C.) for 20 hours and then an additional 8.0 grams peroxide was added (total peroxide = 23.0 grams, 0.16 mole) and the reaction continued for 6 more hours. An olefin analysis of the final reaction mixture indicated 0.46% residual 1-octene by weight, corresponding to 3.1 grams only. The contents were then subjected to vacuum stripping and volatiles boiling up to 170°C. and 40 mm. of Hg. pressure removed. The residue was poured into a one-litre beaker containing 300 mls. of water and heated on a steam bath with occasional stirring. An organic layer formed on top which was extracted twice with ether. The ether layers were combined and evaporated to dryness. The waxy residue thus obtained was placed in 400 mls. of heptane, boiled and filtered. The filtrate was cooled in an ice-water bath and a mass of white crystals obtained. These crystals after drying in a vacuum oven weighed 50 grams, melted at 79—82°C. and had the following elemental analysis:

			Calculated for
			Mono-Octyl Succinic Acid
Element	Found		
Carbon	62.96		62.58
Hydrogen	10.05		9.63
Nitrogen	Nil		0.00

EXAMPLE 2

3-Dodecyl glutarimide

Apparatus: Same as described in Example 1.

The flask was initially purged with nitrogen and then charged as follows:

Glutarimide	=	339.0 grams (3.0 mole)
Hexanol	=	200 mls.
1-Dodecene	=	84.0 grams (0.5 mole)
Di- <i>t</i> -butyl Peroxide	=	15.0 grams (0.1 mole)

The contents were heated and maintained at 130—140°C. for 24 hours. Then, just prior to cooling, a sample was withdrawn and analyzed for 1-dodecene. It contained 0.85% by weight of residual 1-dodecene, corresponding to 5.1 grams only. The contents were then discharged into a one-litre beaker containing 500 mls. of water and stirred on a steam bath for two hours. The hexanol layer was then separated and placed in a 500-ml. reaction flask. The solvent and all other volatiles were stripped in vacuum (150°C./3.0 mm Hg) and the residue cooled and transferred into a one-litre beaker. Petroleum ether (400 mls) was added into the beaker, boiled for several minutes and filtered. The filtrate was then cooled in an ice-water bath for two hours. The resulting white crystalline mass was separated by suction filtration, washed with cold petroleum

- ether and dried in a vacuum oven. The product thus obtained weighed 57.0 grams and melted at 62—65°C. After recrystallizing twice more from petroleum ether it was analyzed as follows:
- Molecular Weight:
Found; 286; Calcd. 281.
- Succinimide = 396.0 grams (4.0 moles)
4-Methylpentene-1 = 84.0 grams (1.0 mole)
Ethyl Alcohol = 200 mls.
t-Butyl Hydroperoxide = 30.0 (0.3 mole)
- % Nitrogen: Found; 5.30; Calcd. 4.97.
- EXAMPLE 3**
3 - (4 - Methylpentyl)succinimide
Apparatus: One-litre stainless steel rocker bomb.
The following ingredients were directly charged into the bomb:
- The bomb was flushed with nitrogen, sealed and heated with shaking. After maintaining at 120—140°C. for 18 hours, it was cooled and the contents discharged into a one-litre distillation flask and all the volatiles removed in vacuum (110°C./25 mm Hg). The residue after cooling (mostly solid) was discharged into a one-litre beaker and about 300 mls of heptane added and then the beaker placed on a steam bath. The contents were maintained at 70—90°C. for half an hour and then suction filtered while hot. The filter cake was once more slurried in hot heptane (200 mls) and filtered. The filtrates were combined, and after reducing the volume by about one-third, it was cooled in ice-water bath. After an hour a mass of white crystals had settled which were separated by suction filtration, washed with cold heptane several times and dried finally in a vacuum oven at 40—50°C. The dried product weighed 75 grams and melted at 85—88°C. After recrystallizing once more from heptane, it was submitted for nitrogen analysis with the following results:
- % Nitrogen: Found, 7.30; Calcd. 7.64.
- EXAMPLE 4**
Apparatus: Same as described in Example 1.
The flask was purged with nitrogen and then the following ingredients charged with continued mild nitrogen pressure on the system:
- Succinimide = 49.5 grams (0.5 mole)
n-Amyl Alcohol = 150.0 grams
- The mixture was stirred and heated till a clear solution was obtained. And then while hot (80—100°C.), the following solution was added within five minutes.
- Chevron C15—20 α -olefins = 244.0 grams (1.0 mole)
(a mixture of cracked wax α -olefins with about 92% terminal unsaturation and an average MW of 244. This product is marketed by California Chemical Company). "Chevron" is a Trade Mark.
- Di-t-butyl Peroxide = 15.0 grams (0.1 mole-initial)
- The resulting solution was further heated and maintained at reflux (135—140°C.). After six hours another 15.0 grams of the peroxide was added (total peroxide = 30 grams, 0.2 mole) and the refluxing continued for 12 more hours. A sample was withdrawn prior to cooling and analyzed. Residual olefin analysis showed 5.9% unsaturation as Chevron C15—20 α -olefins by the weight of the solution, corresponding to 28 grams only. The contents were then subjected to vacuum distillation and all the volatiles boiling up to 140°C. pot temperature at 3.0 mm Hg were stripped. The residue which was a light brown fluid at room temperature weighed 290 grams and was soluble in all hydrocarbons and mineral oils. It was analyzed for nitrogen and found to constitute 2.2% vs. 2.38% for expected. The resulting product was a doubly alkylated succinimide wherein the 3- and 3'-portions contain a mixture of pentadecyl, hexadecyl, octadecyl, nonadecyl and eicosyl groups.
- EXAMPLE 5**
N-Methyl-3-octyl succinimide
Example 1 was repeated with the exception that 4 moles of succinimide were replaced by 4 moles (452 grams) of N-methyl succinimide. The resulting waxy residue was placed in 450 mls of heptane, boiled and filtered. The filtrate was cooled in an ice-water bath

and a mass of white crystals obtained. The crystals, after drying in a vacuum oven, were submitted for nitrogen analysis and molecular weight determination with the following results:

5 % Nitrogen for N-methyl-3-octyl succinimide		
	Calculated	Found
10	6.21	6.45
	Molecular weight	
20	225.31	233.0

EXAMPLE 6

3-Dodecyl diglycolylimide

Example 5 was repeated with the exception that 3 moles of glutarimide were replaced by 3 moles (345 grams) of diglycolylimide. After recrystallizing twice more from petroleum ether, the product was submitted for nitrogen analysis and molecular weight determination with the following results:

20 % Nitrogen for 3-dodecyl diglycolylimide		
	Calculated	Found
25	4.94	5.10
	Molecular Weight	
25	238.39	277.0

The alkylated imides may be vinylated but the potassium salt should first be formed by mixing the alkylated compound with about 2% by weight of powdered caustic potash and distilling off the water formed before doing so. They can then be vinylated at about 15 atmospheres of pressure with a mixture of acetylene and nitrogen in the conventional manner. The resulting monomers polymerize by the conventional solution polymerization to yield homopolymers having solubility in a wide range of polar and non-polar solvents. The solubility can be systematically controlled during the alkylation reaction, by choosing both the type of α -olefin used and the amount thereof. After vinylation, homopolymers are obtained which are still soluble in polar solvents (such as alcohols) as well as those having intermediate degrees of solubility between polar and non-polar solvents. Homopolymers with a low degree of alkylation are still soluble in ethanol so that they can be formulated with "Freon" propellants to yield hair sprays whose sensitivity to moisture is thereby reduced. "Freon" is a Trade Mark. Homopolymers with a high degree of alkylation are soluble in aliphatic hydrocarbons, mineral and lubricating oils. In the latter case, they are useful as sludge dispersants and viscosity index improvers for lubricating oils. This is in contrast to homopolymers prepared from non-alkylated N-vinyl imides which are insoluble in aliphatic hydrocarbons, mineral oils and lubricating oils.

The alkylated cyclic imides are especially useful for incorporation into polyalkylene plastics such as polyethylene, polypropylene and polybutene to improve the dye receptivity thereof either in sheet form, fibre or fabric.

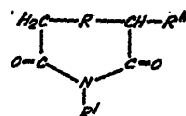
The alkylated 5- or 6-membered cyclic imides when alkylated in accordance with the invention with α -olefins of from 8 to 42 carbon atoms yield alkylates which are useful as ashless dispersants for engine oils and as rust inhibitors in a variety of lubricating oils, including engine oils.

Allyl alcohol or allyl cyanide may be used as the hydroxy or cyano derivative of an α -olefin in the process of the present invention. When allyl alcohol is used, the hydroxy function is introduced making possible further reaction to many useful derivatives. When allyl cyanide is used, the nitrile group introduced can be converted to amide or carboxyl, making possible many other useful derivatives.

The alkylated cyclic imides prepared as above in which the nitrogen atom is unsubstituted are excellent starting materials for the preparation of *m*-nitro benzyl derivatives. In this preparation 1 mole of each of alkylated cyclic imide, formaldehyde or paraformaldehyde, and a substituted or unsubstituted nitrobenzene in which one of the *meta* positions to the nitro group is unoccupied (e.g. *p*-nitrotoluene, *p*-chloronitrobenzene or 1,3-dimethyl-4-nitrobenzene) are condensed in the presence of sulfuric acid in accordance with the procedure outlined in U.S. Patent Specification 2,652,403. After reduction to the corresponding *m*-amino benzyl derivatives, there are obtained products which are valuable dye intermediates.

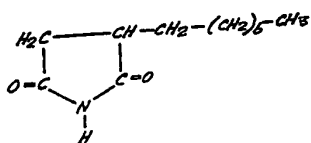
WHAT WE CLAIM IS:—

1. The alkyl-substituted cyclic imide of the general formula:

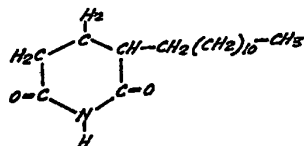


wherein R represents a single bond or an oxy or a methylene group, R' represents hydrogen, an alkyl group from 2 to 18 carbon atoms inclusive, a hydroxyl alkyl group or an alkylaminoalkyl group wherein the alkyl contains from 1 to 6 carbon atoms inclusive, and R'' represents an alkyl group of from 8 to 42 carbon atoms inclusive.

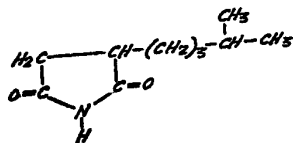
2. 3-Octyl succinimide having the following formula:



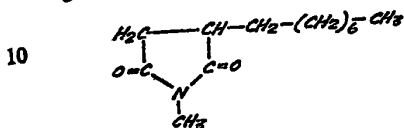
3. 3-Dodecyl glutarimide having the following formula:



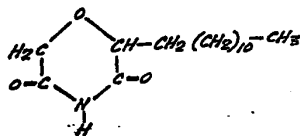
4. 3 - (4 - Methylpentyl) - succinimide having the following formula:



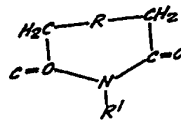
5. N - methyl - 3 - octyl succinimide having the following formula:



6. 3-Dodecyl diglycolylimide having the following formula:



7. A process for the preparation of alkylated cyclic imides which comprises heating at a pressure in excess of atmospheric pressure from 0.01 to 10 molar proportions of an α -olefin of at least 2 carbon atoms, or a halo, hydroxy or cyano derivative thereof, with one molar proportion of a cyclic imide having the following general formula:



wherein R represents a single bond joining the two methylene groups, an oxy or a methylene group and R' represents hydrogen, an alkyl group of from 2 to 18 carbon atoms inclusive, a hydroxy alkyl group or an alkylaminoalkyl group wherein the alkyl contains from 1 to 6 carbon atoms inclusive, at a temperature of from 100°C-200°C. in the presence of from 0.02 to 0.3 molar proportion of an organic peroxide per mole of the said α -olefin or a derivative thereof.

8. The process claimed in Claim 7, in which the cyclic imide is N-methyl succinimide.

9. The process claimed in Claim 7, in which the cyclic imide is diglycolylimide.

10. The process claimed in Claim 7, in which the cyclic imide is glutarimide.

11. The process claimed in Claim 7, in which the cyclic imide is succinimide.

12. The process claimed in any one of Claims 7 to 9, in which the α -olefin is α -octene.

13. The process claimed in any one of Claims 7 to 9, in which the α -olefin is α -dodecene.

14. The process claimed in any one of Claims 7 to 9, in which the α -olefin is 4-methylpentene-1.

15. The process claimed in any one of Claims 7 to 9, in which the organic peroxide is *t*-butyl hydroperoxide.

16. The process claimed in any one of Claims 7 to 9, in which the organic peroxide is di-*t*-butyl peroxide.

17. The process for the preparation of alkylated cyclicimides substantially as herein described with reference to any one of Examples 1 to 6.

18. Alkylated cyclic imides whenever prepared or produced by the process claimed in any one of Claims 7 to 17.

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